

# Relativistic effects in gold chemistry. VI. Coupled cluster calculations for the isoelectronic series $\text{AuPt}^-$ , $\text{Au}_2$ , and $\text{AuHg}^+$

Ralf Wesendrup, Jon K. Laerdahl, and Peter Schwerdtfeger<sup>a)</sup>

*Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand*

(Received 16 December 1998; accepted 11 February 1999)

Nonrelativistic and scalar relativistic pseudopotential calculations were carried out for the isoelectronic series of diatomic molecules  $\text{AuPt}^-$ ,  $\text{Au}_2$ , and  $\text{AuHg}^+$  at the Hartree–Fock, second-order Møller–Plesset (MP2), and coupled-cluster [CCSD(T)] level. For  $\text{Au}_2$  we performed large scale fully relativistic Dirac–Hartree–Fock and MP2 benchmark calculations in order to test the reliability of the pseudopotential approximation. Both methods yield almost identical spectroscopic properties for  $\text{Au}_2$ . The comparison further reveals that pseudopotentials correctly describe the effects of relativity on the spectroscopic properties of  $\text{Au}_2$ . The yet unknown diatomic species  $\text{AuPt}^-$  and  $\text{AuHg}^+$  are stable compounds, and their rotational–vibrational constants are predicted. These show striking similarities compared to the values of  $\text{Au}_2$ . MP2 results including a set of three  $g$ -functions per metal atom indicate that higher angular momentum functions are important for accurately predicting the bond distance of these molecules. © 1999 American Institute of Physics. [S0021-9606(99)30718-2]

## I. INTRODUCTION

Across a row of the periodic table relativistic effects are at their maximum at the group 11 elements Cu, Ag, Au,<sup>1,2</sup> and the heaviest homolog in this series, element 111.<sup>3</sup> The underlying reason is not so well understood, but it is assumed that the filling of the lower  $d$  shell might be responsible for the outstanding behavior of the group 11 elements. As a result, relativistic effects cannot be neglected anymore even for the lightest element in this series, copper.<sup>4</sup> For gold, relativistic effects often exceed the effects of electron correlation and both the physics and chemistry of gold are dominated by relativistic effects.<sup>5–7</sup> For compounds of the neighboring elements platinum and mercury, relativistic effects are still large,<sup>8</sup> but are expected to be smaller compared to similar compounds of gold.

The gold dimer  $\text{Au}_2$  has been the subject of many theoretical studies.<sup>6–20</sup> The special interest in this simple diatomic molecule is mainly stimulated by the relativistic  $6s$  contraction in gold which causes a large bond contraction and leads to the well known anomaly in the bond lengths,  $r_e(\text{Cu}_2) < r_e(\text{Au}_2) < r_e(\text{Ag}_2)$ .<sup>21</sup> The majority of recent studies using various relativistic techniques and electron correlation procedures predict a relativistic bond contraction between 0.18 and 0.30 Å for  $\text{Au}_2$  (Fig. 1).

The most widely used method in heavy element calculations is the relativistic pseudopotential approximation. This method is still criticized by a few authors<sup>22</sup> since differently adjusted pseudopotentials together with the supplied standard basis sets can lead to quite different results for molecular properties.<sup>23</sup> However, a careful adjustment of the pseudopotential parameters together with a reasonably small core definition and energy optimized basis sets leads to er-

rors which are smaller than the usual errors of basis set incompleteness and limitations in the electron correlation procedure applied.<sup>24</sup> This has recently been demonstrated by our group for the example of  $\text{AuH}$ .<sup>25</sup>

In this article we study in detail relativistic effects in molecular properties of  $\text{Au}_2$  at the scalar relativistic pseudopotential level using energy adjusted Stuttgart pseudopotentials together with large valence basis sets. Electron correlation effects are treated at the coupled cluster, CCSD(T), and Møller–Plesset level, MP2. The results are compared to benchmark fully relativistic four-component calculations at the Dirac–Hartree–Fock (DHF) and MP2 level of theory. For comparison, scalar relativistic calculations are carried out for the isoelectronic species  $\text{AuPt}^-$  and  $\text{AuHg}^+$ . Earlier investigations on these molecules are not known to the authors,<sup>26,27</sup> and the predicted spectroscopic parameters may be used for future identification.

## II. COMPUTATIONAL DETAILS

For the nonrelativistic (NRPP) and scalar relativistic pseudopotential (SRPP) Hartree–Fock (HF), second-order Møller–Plesset (MP2), and coupled cluster calculations [CCSD and CCSD(T)] calculations we used energy consistent pseudopotentials to replace the 60 inner electrons of Pt, Au, and Hg.<sup>6,20</sup> The orbital space was kept fully active in the correlated calculations. For gold we used the  $(9s\ 7p\ 6d\ 3f)/[8s\ 4p\ 5d\ 3f]$  basis sets as described in Ref. 28, decontracted all but the two highest  $p$  exponents and added a  $(2s\ 1p\ 2d\ 1f)$  set of diffuse functions. For Pt we optimized a  $(11s\ 10p\ 7d)/[9s\ 7p\ 5d]$  basis sets by minimizing the total energy at the Hartree–Fock level (HF) and added the same set of diffuse and  $f$  functions as in the case of gold. For Hg the  $(7s\ 7p\ 5d)/[6s\ 6p\ 4d]$  basis sets of Ref. 29 were augmented by four  $f$  functions and a set of diffuse functions to match the size and the most diffuse exponents of

<sup>a)</sup>Electronic mail: schwerd@ccul.auckland.ac.nz

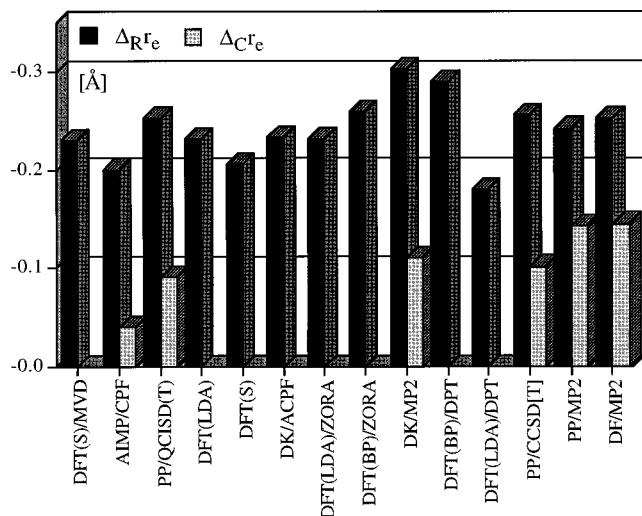


FIG. 1. Published bond length contractions in  $\text{Au}_2$  due to relativistic and correlation contributions. From the left to the right: DFT(S)/MVD from Ziegler *et al.* (Ref. 19), AIMP/CPF from Strömberg and Wahlgren (Ref. 12), PP/QCISD(T) from Schwerdtfeger (Ref. 7), DFT(LDA) from Häberlen and Rösch (Ref. 11), DFT(S) from Bastug *et al.* (Ref. 16), DK/ACPF from Hess (Ref. 17), DFT(LDA)/ZORA and DFT(BP)/ZORA from van Lenthe *et al.* (Ref. 14), DK/MP2 from Park und Almlöf (Ref. 10), DFT(BP)/DPT and DFT(LDA)/DPT from van Wüllen (Ref. 18), PP/CCSD(T), PP/MP2 and four-component MP2 (RMP2) from this work.

Au and Pt. This results in the following contraction schemes:  $(13s\ 11p\ 9d\ 4f)/[11s\ 8p\ 7d\ 4f]$  for Pt,  $(11s\ 9p\ 8d\ 4f)/[10s\ 8p\ 7d\ 4f]$  for Au, and  $(10s\ 9p\ 8d\ 4f)/[9s\ 7p\ 6d\ 4f]$  for Hg at the nonrelativistic level;  $(13s\ 11p\ 9d\ 4f)/[11s\ 8p\ 7d\ 4f]$  for Pt,  $(10s\ 8p\ 7d\ 4f)/[9s\ 7p\ 6d\ 4f]$  for Au, and  $(11s\ 10p\ 8d\ 4f)/[10s\ 9p\ 7d\ 4f]$  for Hg at the relativistic level. The quality of our basis sets used can be estimated from the calculated electron affinities and ionization potentials for the neutral elements at the coupled cluster level of theory which are in very good agreement with experimental results (Table I).<sup>30</sup> The additional set of three  $g$  functions used for the extended MP2 calculations for  $\text{Au}_2$  was chosen to match the three high exponent  $f$  functions. The calculations were performed with the GAUSSIAN94 and ACES2 program packages.<sup>31,32</sup> Up to 20 single points were calculated at the different levels of theory to describe the most important part of the potential energy curve for the diatomic molecules. A rotational–vibrational analysis to obtain rovibrational

TABLE I. Vertical atomic ionization potentials (IP) and electron affinities (EA) calculated at the CCSD(T) level.<sup>a</sup>

		Pt	Au	Hg
IP	NRPP	7.04 <sup>b</sup>	7.05	8.32
	SRPP	8.93 <sup>c</sup>	9.02	10.32
	exp. <sup>d</sup>	9.00	9.23	10.44
EA	NRPP	0.00 <sup>b</sup>	1.17	0.00
	SRPP	2.07 <sup>c</sup>	2.19	0.00
	exp. <sup>d</sup>	2.12	2.31	0.00

<sup>a</sup>All values in units of eV.

<sup>b</sup>Related to the Pt ( $6s^0\ 5d^{10}$ ) ground state in the nonrelativistic calculation.

<sup>c</sup>Not corrected for spin-orbit coupling.

<sup>d</sup>Experimental values from Ref. 30.

wave functions and eigenstates was then carried out applying the numerical Numerov–Cooley procedure as implemented in the MOLCAS2 program package.<sup>33</sup>

The all-electron relativistic four-component Dirac–Hartree–Fock (DHF) and MP2 calculations were performed with the DIRAC program suite.<sup>34–36</sup> The DHF calculations for Au were performed with the open-shell module that recently has been developed by Thyssen.<sup>37</sup> The open-shell MP2 energy was calculated with Visscher’s RELCCSD code.<sup>38</sup> This program has been interfaced with DIRAC. For the four-component DHF calculations the original gold basis set by Laerdahl *et al.*<sup>35</sup> was modified in the core region and in the  $s$ -type valence space. The two (three) high exponent  $s(p)$  functions were replaced by an even-tempered series of three (six) functions (ratio 4.0). The two low exponent  $s$  functions were replaced by an even-tempered series of four functions (ratio 2.5). The energy of the final dual family ( $25s\ 23p\ 14d\ 10f$ ) basis set is 0.058 a.u. above the numerical DHF limit. The relativistic calculations were performed with a Gaussian nuclear model. The nuclear exponent and atomic DHF limit energy is given by Visscher and Dyall.<sup>39</sup> Test calculations show that the remaining deficiency in the basis set is in the core region which is of little importance for the chemical properties considered in this study. The resulting Gaussian basis set has been used in spherical and uncontracted form for the large component functions, and the small component basis sets were generated from the large component set using a linear transformation and a projection<sup>40</sup> that is equivalent to the restricted kinetic balance (RKB) condition.<sup>41</sup> The total number of functions used is 468 for the large component in  $\text{Au}_2$ . To our knowledge this represents the largest fully relativistic correlated calculations carried out so far. All the 38 valence and subvalence electrons of  $\text{Au}_2$  were correlated in the direct MP2 calculations. Note that the  $5s$  orbital of Au is energetically below the  $4f$  shell in the relativistic case. The  $4f$  orbitals were not correlated in the calculations. Virtual orbitals above 100 a.u. were neglected, and the sum over molecular orbitals in the second-order perturbation term was restricted to positive energy eigenstates of the DHF solutions. (SS | SS) two-electron integrals were included in the DHF calculations, but neglected in the calculation of the MP2 energy. This is known to have negligible effects on spectroscopic properties.<sup>35,36</sup> The force constants were calculated from a quadratic fit to three points at exactly  $r=r_e$  and  $r=r_e \pm 0.01\ \text{Å}$ . The all-electron nonrelativistic calculations were carried out using GAUSSIAN94.<sup>31</sup>

### III. RESULTS AND DISCUSSION

The calculated spectroscopic constants for the  $1^1\Sigma^+$  ground states of  $\text{AuPt}^-$ ,  $\text{Au}_2$ , and  $\text{AuHg}^+$  are listed in Table II and show an excellent agreement of the pseudopotential with the all-electron HF or MP2 results. In both the nonrelativistic and relativistic treatment there is almost numerical identity of the calculated bond distances and vibrational frequencies. As spin–orbit coupling is explicitly included in the fully relativistic calculations while the scalar relativistic pseudopotentials are spin–orbit averaged, the agreement of both relativistic methods also confirms the comparatively small effects of spin–orbit coupling in  $\text{Au}_2$ . To check if this

TABLE II. Spectroscopic properties for the electronic ground states ( $^1\Sigma^+$ ) of the isoelectronic molecules AuPt<sup>-</sup>, Au<sub>2</sub>, and AuHg<sup>+</sup>.<sup>a</sup>

		AuPt <sup>-</sup>		Au <sub>2</sub>				HgAu <sup>+</sup>	
		NRPP	SRPP	NRPP	AENR	SRPP	AEFR	NRPP	SRPP
$r_e$	HF	3.102	2.674	2.930	2.930	2.606	2.594	3.066	2.700
	MP2	2.751	2.425	2.696	2.701	2.454	2.449	2.794	2.528
	CCSD	2.830	2.521	2.771		2.510		2.880	2.590
	CCSD(T)	2.801	2.517	2.761		2.505		2.863	2.581
	CCSD(T)+g(MP2)		2.494			2.486			2.562
$D_e$	HF	0.292	0.140	0.400	0.384	0.833	0.895	0.931	1.238
	MP2	1.313	2.832	1.606	1.566	2.531	2.544	1.512	2.044
	CCSD	0.978	1.788	1.246		2.001		1.292	1.747
	CCSD(T)	1.161	2.182	1.414		2.219		1.370	1.857
	CCSD(T)+g(MP2)		2.149			2.212			1.921
IP	HF	0.44 <sup>b</sup>	0.00	5.26		7.17		11.82	14.30
	MP2	1.66	2.46	7.30		9.78		14.02	16.72
	CCSD	1.52	1.76	6.89		9.08		13.59	16.08
	CCSD(T)	1.65	2.07	7.08		9.11		13.70	16.11
$\omega_e$	HF	72	93	98	97	160	159	78	119
	MP2	120	203	140	140	205	205	115	167
	CCSD	101	171	125		185		100	147
	CCSD(T)	103	176	125		182		97	139
	CCSD(T)+g(MP2)		172			189			165
$\omega_e x_e$	CCSD(T)	0.60	0.36	0.59		0.47		0.11	0.36
$B_e$	CCSD(T)	0.219	0.274	0.225		0.273		0.206	0.253
$D_e$	CCSD(T)	0.379	0.466	0.296		0.252		0.374	0.330
$\alpha_e$	CCSD(T)	0.83	0.60	0.86		0.71		0.57	0.47

<sup>a</sup>NRPP: nonrelativistic pseudopotential, SRPP: scalar relativistic pseudopotential, AENR: all-electron nonrelativistic, AEFR: four-component all-electron fully relativistic. CCSD(T)+g(MP2) are CCSD(T) results corrected for the contribution of  $g$  functions at the MP2 level. Calculated bond distances  $r_e$  in Å, bond dissociation energies,  $D_e$  (not corrected for vibrational contributions) relative to the lowest calculated energy dissociation channels in eV, vertical ionization energies, IP, in eV, harmonic frequencies  $\omega_e$  in  $\text{cm}^{-1}$ , anharmonicity constant  $\omega_e x_e$  in  $\text{cm}^{-1}$ , rotational constant  $B_e$  in  $10^{-1} \text{cm}^{-1}$ , centrifugal distortion constant  $D_e$  in  $10^{-8} \text{cm}^{-1}$ , vibration-rotational coupling constant  $\alpha_e$  in  $10^{-4} \text{cm}^{-1}$ . The experimental values for the Au<sub>2</sub> dimer are  $r_e = 2.472 \text{Å}$ ,  $D_e = 2.36 \text{eV}$ ,  $\text{IP} = 9.5 \pm 0.3 \text{eV}$ ,  $\omega_e = 191 \text{cm}^{-1}$ ,  $\omega_e x_e = 0.420 \text{cm}^{-1}$ ,  $B_e = 0.28 \times 10^{-1} \text{cm}^{-1}$ ,  $D_e = 0.250 \times 10^{-8} \text{cm}^{-1}$ ,  $\alpha_e = 0.723 \times 10^{-4} \text{cm}^{-1}$  (Ref. 21).

<sup>b</sup>The adiabatic ionization energy is 0 eV at the HF level.

agreement might be due to a fortunate error cancellation in the applied basis sets we repeated the relativistic pseudopotential calculations using the outer functions of the all-electron basis sets (BS2=11s 10p 7d 5f) (Table III). With the notable exception of the MP2 bond energy both basis sets yield almost identical results, thus supporting the values obtained with BS1. The error introduced by the pseudopotential approximation is obviously minor compared to errors due to basis set and electron correlation incompleteness.

Experimental data are available only for Au<sub>2</sub>,<sup>21</sup> and our highest level correlated scalar relativistic pseudopotential calculations agree well with these data. Note that our coupled cluster Au<sub>2</sub> bond distance (and most other Au<sub>2</sub> bond distances calculated so far)<sup>6-20</sup> is  $\sim 0.03 \text{Å}$  above the experimental value of  $2.47 \text{Å}$ . A small decrease in the Au<sub>2</sub> bond length is obtained when spin-orbit coupling is included in the relativistic treatment. For instance, the four-component DHF and MP2 calculations show a  $0.01 \text{Å}$  larger relativistic bond contraction compared to the scalar pseudopotential results. This value nicely matches a recent analysis on spin-orbit effects in Au<sub>2</sub> by Lee *et al.* who showed within a Kramers restricted two-component relativistic pseudopotential approach that spin-orbit effects diminish the Au<sub>2</sub> bond length by  $\Delta_{\text{SO}} r_e = -0.004 \text{Å}$  at the MP2 or CCSD(T) level.<sup>9</sup> Very similar small effects are found for the harmonic fre-

quency,  $\Delta_{\text{SO}} \omega_e = 1 \text{cm}^{-1}$ , and the dissociation energy,  $\Delta_{\text{SO}} D_e = 0.05 \text{eV}$ .<sup>9</sup> This agrees remarkably well with  $\Delta \omega_e = 0 \text{cm}^{-1}$  and  $\Delta D_e = 0.052 \text{eV}$  in our study, even if the difference between the pseudopotential and the four-component calculations is not a direct measure for the effect of spin-orbit coupling. Adding the spin-orbit correction to our coupled cluster result gives a internuclear distance of  $\sim 2.50 \text{Å}$  which is still too high. We therefore added a set of three  $g$  functions at the MP2 level to estimate the effect of basis set incompleteness (Table III, BS1+g) which further reduces

TABLE III. Comparison of calculated scalar relativistic bond distances,  $r_e$ , dissociation energies,  $D_e$ , and harmonic vibrational frequencies,  $\omega_e$ , for Au<sub>2</sub> using different basis sets.<sup>a</sup>

	BS1		BS1+g		BS2	
	SCF	MP2	SCF	MP2	SCF	MP2
$r_e$	2.606	2.454	2.599	2.435	2.605	2.450
$D_e$	0.833	2.531	0.852	2.524	0.831	2.453
$\omega_e$	160	205	156	212	162	205

<sup>a</sup> $r_e$  in Å,  $D_e$  in eV, and  $\omega_e$  in  $\text{cm}^{-1}$ . BS1 denotes the standard basis set employed in the coupled cluster calculations, BS1+g is augmented by three  $g$  functions, and BS2 is the outer 11s 10p 7d 5f functions of the all-electron fully relativistic basis set.

the bond distance by 0.019 Å. A similar effect is expected for the coupled cluster results and the extrapolated values are included in Table II as CCSD(T)+g(MP2). We therefore conclude that relatively large basis sets with high angular momentum functions are required to converge towards the experimental bond distance of 2.47 Å at the CCSD(T) level.

There is excellent agreement between all-electron and pseudopotential calculations for relativistic and correlation contributions in the spectroscopic constants of Au<sub>2</sub>. The relativistic bond contraction at the MP2 level corresponds to -0.242 Å for the pseudopotential and -0.252 Å for the all-electron calculation, the correlation contraction in the relativistic case to -0.152 Å and -0.145 Å, respectively. Previous published results yield a relativistic bond contraction between -0.18 Å and -0.32 Å. An overview is given in Fig. 1 together with a comparison to our results, which we expect to accurately describe relativistic changes within 5%. At the CCSD(T) level we attribute the following changes in Au<sub>2</sub> to relativistic effects:  $\Delta_R r_e = -0.26$  Å,  $\Delta_R D_e = 0.86$  eV,  $\Delta_R IP = 2.0$  eV and  $\Delta_R \omega_e = 57$  cm<sup>-1</sup>. In comparison, changes due to electron correlation at the relativistic level amount to:  $\Delta_C r_e = -0.10$  Å,  $\Delta_C D_e = 1.4$  eV,  $\Delta_C IP = 2.0$  eV, and  $\Delta_C \omega_e = 19$  cm<sup>-1</sup>. In conclusion, relativistic effects are of equal importance or even exceed the effects of electron correlation as indicated previously.<sup>6</sup> Moreover, the results clearly demonstrate that electron correlation and relativistic effects are not additive (see Table II).

To our knowledge, the two isoelectronic compounds AuPt<sup>-</sup> and AuHg<sup>+</sup> are not yet known, and of related compounds only AuPt and AuPt<sup>+</sup> have been investigated before.<sup>42</sup> Dai and Balasubramanian obtained for the <sup>2</sup>Δ<sub>5/2</sub> ground state of AuPt  $r_e = 2.544$  Å,  $\omega_e = 194$  cm<sup>-1</sup>, and  $D_e$  between 2.2 and 2.7 eV. Interestingly, the addition of another electron to AuPt does not increase the bond distance as one might expect for an anion. In contrast, according to our calculations the bond distance decreases from 2.544 Å for AuPt at the MRSDCI level<sup>42</sup> to 2.517 Å for AuPt<sup>-</sup> at the CCSD(T) level and is even further reduced by the addition of three *g* functions. While this difference may partly be ascribed to the different methods used, it is an indication of the bonding character of the  $\sigma$  HOMO in AuPt<sup>-</sup>. Note that this is in perfect analogy to the bond length reduction from Au<sub>2</sub><sup>+</sup> to Au<sub>2</sub> or even for linear Au<sub>3</sub> and Au<sub>3</sub><sup>-</sup>.<sup>43</sup> Still it remains somewhat surprising that AuPt<sup>-</sup> appears to be as tightly bound as Au<sub>2</sub> at the scalar relativistic coupled cluster level. In general, the similarities between AuPt<sup>-</sup>, Au<sub>2</sub>, and AuHg<sup>+</sup> in the molecular properties studied here are quite-striking. For example, after correction for the effect of additional *g*-functions (Table III) one obtains the following bond distances at the CCSD(T) level:  $r_e(\text{AuPt}^-) = 2.494$  Å,  $r_e(\text{Au}_2) = 2.486$  Å,  $r_e(\text{AuHg}^+) = 2.562$  Å. In parallel, bond dissociation energies only vary slightly from 1.921 eV for AuHg<sup>+</sup> to 2.212 eV for Au<sub>2</sub>. The only major difference between the three isoelectronic species is the first ionization potential which, as expected, increases sharply with the charge of the molecule from ~2 eV in AuPt<sup>-</sup> to >16 eV in AuHg<sup>+</sup>.

The quite significant relativistic changes in the bond distance, dissociation energy, and force constant are shown in Fig. 2 for the three isoelectronic species. Note, that our

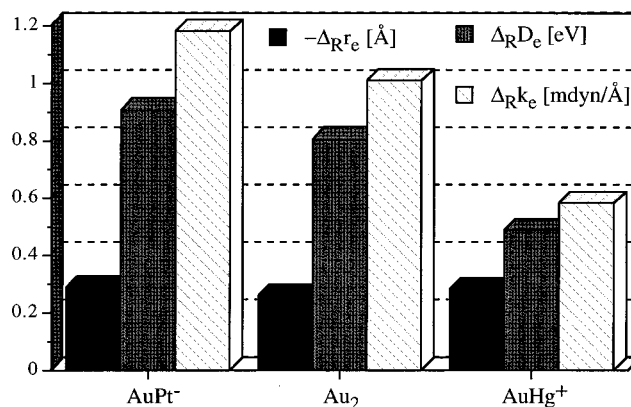
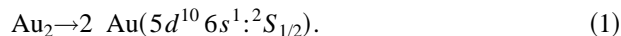
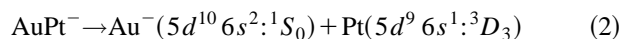


FIG. 2. Relativistic changes in bond distances,  $r_e$ , dissociation energies,  $D_e$ , and force constants,  $k_e$ , for AuPt<sup>-</sup>, Au<sub>2</sub>, and AuHg<sup>+</sup> at the pseudopotential CCSD(T) level. The dissociation energy for AuPt<sup>-</sup> is corrected for atomic spin-orbit coupling ( $\Delta_{SO} D_e = -0.25$  kJ mol<sup>-1</sup>).

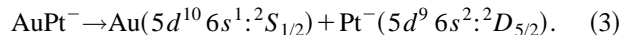
coupled cluster bond energy has to be corrected for spin-orbit coupling in the platinum atom (ground state: <sup>3</sup>D<sub>3</sub>) or anion (ground state: <sup>2</sup>D<sub>5/2</sub>) which reduces the bond strength by ~0.2–0.4 eV.<sup>44</sup> Yet it remains surprising that the relativistic effects for AuPt<sup>-</sup> are similar or even larger than the ones in Au<sub>2</sub> considering a relativistic group 11 maximum.<sup>1</sup> A possible explanation is provided by the different dissociation reactions for the three molecules. At both the relativistic and nonrelativistic level dissociation of the gold dimer occurs according to



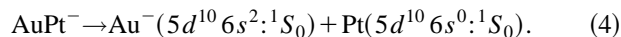
For AuPt<sup>-</sup> the situation is more complicated. At the relativistic level the least endothermic dissociation yields the gold anion and neutral platinum



in agreement with the experimental atomic data.<sup>30</sup> However, the interaction of the closed shell gold anion with the platinum atom can hardly account for the strong bond in AuPt<sup>-</sup>. As the electron affinity of both elements differs only slightly, a second low lying dissociation channel becomes feasible to give rise to the neutral gold atom and a platinum anion:

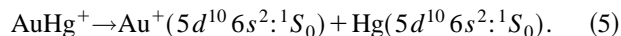


Accordingly, AuPt<sup>-</sup> would best be described as a gold atom and a platinum anion which form a strong  $\sigma$  bond. Indeed, a Mulliken population analysis of AuPt<sup>-</sup> reveals that the negative charge is located at the platinum center in line with the given interpretation. At the nonrelativistic level, however, the electronic ground state of platinum is a singlet and does not even exhibit a positive electron affinity. Thus, in the nonrelativistic case the molecule dissociates preferably as



The major contribution to the bonding is therefore of the two closed shell atoms interacting in AuPt<sup>-</sup> resulting in a drastic weakening of the bond compared to the relativistic calculations.

In analogy,  $\text{AuHg}^+$  might either be described as two interaction closed shell species or two open shell atoms forming a  $\sigma$  bond. According to the higher ionization potential of Hg compared to Au the lowest energy dissociation channel is



While a Mulliken population analysis shows that the positive charge is mostly located at the gold atom, the interaction of  $\text{Au}^+$  with the highly polarizable mercury atom cannot account for the bond energy of  $>1.8$  eV and covalent contributions must be present.<sup>45</sup> In the nonrelativistic case the difference in ionization energies between gold and mercury is conserved and the contribution of the ionic and the covalent form will be similar as in the relativistic case. Thus, the relativistic changes in  $\text{AuHg}^+$  are less pronounced than in  $\text{Au}_2$  and  $\text{AuPt}^-$ .

## ACKNOWLEDGMENTS

The authors thank J. Thyssen for providing us with a copy of the open-shell module of the DIRAC program prior to publication. We are grateful to the Deutsche Forschungsgemeinschaft (DFG) for a postdoctoral grant for R.W., to the Marsden Fund Wellington (Contract No. 96-UOA-PSE-0081), the Royal Society of New Zealand, and the Auckland University Research Committee for financial support, and the Norwegian Research Council (Program for Supercomputing) for generously providing computational time.

- <sup>1</sup>P. Pyykkö and J. P. Desclaux, *Acc. Chem. Res.* **12**, 276 (1979).  
<sup>2</sup>P. Pyykkö, *Chem. Rev.* **88**, 563 (1988).  
<sup>3</sup>(a) B. Fricke, *Struct. Bonding (Berlin)* **21**, 89 (1975); (b) E. Eliav, U. Kaldor, P. Schwerdtfeger, B. A. Hess, and Y. Ishikawa, *Phys. Rev. Lett.* **73**, 3203 (1994); (c) B. A. Hess, *Ber. Bunsenges. Phys. Chem.* **101**, 1 (1997); (d) M. Seth, P. Schwerdtfeger, and M. Dolg, *J. Chem. Phys.* **106**, 3623 (1997).  
<sup>4</sup>I. Antes and G. Frenking, *Organometallics* **14**, 4263 (1995).  
<sup>5</sup>(a) P. Schwerdtfeger, *J. Am. Chem. Soc.* **111**, 7261 (1989); (b) P. Schwerdtfeger, P. D. W. Boyd, A. K. Burrell, W. T. Robinson, and M. J. Taylor, *Inorg. Chem.* **29**, 3593 (1990); (c) P. Schwerdtfeger, *Phys. Rev. A* **43**, 1644 (1991); (d) P. Schwerdtfeger, P. D. W. Boyd, S. Brienne, and A. K. Burrell, *Inorg. Chem.* **31**, 3411 (1992); (e) P. Schwerdtfeger and G. A. Bowmaker, *J. Chem. Phys.* **100**, 4487 (1994); (f) I. Antes, S. Dapprich, G. Frenking, and P. Schwerdtfeger, *Inorg. Chem.* **35**, 2089 (1996); (g) P. Pyykkö, *Chem. Rev.* **97**, 597 (1997); (h) P. Pyykkö and F. Mendizabal, *Inorg. Chem.* **37**, 3018 (1998); (i) R. Franke and C. van Wüllen, *J. Comput. Chem.* **19**, 1596 (1998); (j) M. Ilias, P. Furdik, and M. Urban, *J. Phys. Chem.* **102**, 5263 (1998).  
<sup>6</sup>P. Schwerdtfeger, M. Dolg, W. H. E. Schwarz, G. A. Bowmaker, and P. D. W. Boyd, *J. Chem. Phys.* **91**, 1762 (1989).  
<sup>7</sup>P. Schwerdtfeger, *Chem. Phys. Lett.* **183**, 457 (1991).  
<sup>8</sup>U. Wahlgren, B. Schimmelpfennig, S. Jusuf, H. Strömsnes, O. Gropen, and L. Maron, *Chem. Phys. Lett.* **287**, 525 (1998).  
<sup>9</sup>H.-S. Lee, Y.-K. Han, M. C. Kim, C. Bae, and Y. S. Lee, *Chem. Phys. Lett.* **293**, 97 (1998).  
<sup>10</sup>C. Park and J. E. Almlöf, *Chem. Phys. Lett.* **231**, 269 (1994).  
<sup>11</sup>O. D. Häberlen and N. Rösch, *Chem. Phys. Lett.* **199**, 491 (1992).  
<sup>12</sup>D. Strömberg and U. Wahlgren, *Chem. Phys. Lett.* **169**, 109 (1990).  
<sup>13</sup>P. Pyykkö and J. P. Desclaux, *C. R. Acad. Sci. Paris* **293**, 1513 (1981).  
<sup>14</sup>E. van Lenthe, E. J. Baerends, and J. G. Snijders, *J. Chem. Phys.* **101**, 9783 (1994).  
<sup>15</sup>(a) Y. S. Lee, W. C. Ermler, K. S. Pitzer, and A. D. McLean, *J. Chem. Phys.* **70**, 288 (1979); (b) W. C. Ermler, Y. S. Lee, and K. S. Pitzer, *ibid.* **70**, 293 (1979); (c) T. Ziegler, J. G. Snijders, and E. J. Baerends, *ibid.* **74**, 1271 (1981); (d) K. S. Pitzer, *Int. J. Quantum Chem.* **25**, 131 (1984); (e) S. Rabii and C. Y. Yang, *Chem. Phys. Lett.* **105**, 480 (1984); (f) P. A. Christiansen and W. C. Ermler, *Mol. Phys.* **55**, 1109 (1985); (g) R. B. Ross and W. C. Ermler, *J. Phys. Chem.* **89**, 5202 (1985); (h) S. P. Walch, C. W. Bauschlicher, and S. R. Langhoff, *J. Chem. Phys.* **85**, 5900 (1986); (i) K. Balasubramanian, *J. Phys. Chem.* **93**, 6585 (1989); (j) K. Balasubramanian, P. Y. Feng, and M. Z. Liao, *J. Chem. Phys.* **93**, 3561 (1989); (k) C. W. Bauschlicher, S. R. Langhoff, and H. Partridge, *ibid.* **91**, 2412 (1989); (l) K. Balasubramanian and P. Y. Feng, *Chem. Phys. Lett.* **159**, 452 (1989); (m) C. W. Bauschlicher, *ibid.* **156**, 91 (1989); (n) P. Ballone and G. Galli, *Phys. Rev. B* **42**, 1112 (1990); (o) C. W. Bauschlicher, S. R. Langhoff, and H. Partridge, *J. Chem. Phys.* **93**, 8133 (1990); (p) H. Partridge, C. W. Bauschlicher, and S. R. Langhoff, *Chem. Phys. Lett.* **175**, 531 (1990); (q) K. K. Das and K. Balasubramanian, *J. Mol. Spectrosc.* **140**, 280 (1990); (r) P. Pyykkö and N. Runeberg, *J. Chem. Soc. Chem. Commun.* **1993**, 1812; (s) M. Mayer, O. D. Häberlen, and N. Rösch, *Phys. Rev. A* **54**, 4775 (1996); (t) V. A. Nasluzov and N. Rösch, *Chem. Phys.* **210**, 413 (1996).  
<sup>16</sup>T. Bastug, D. Heinemann, W. D. Sepp, and B. Fricke, *Chem. Phys. Lett.* **211**, 119 (1993).  
<sup>17</sup>B. Hess (private communication).  
<sup>18</sup>C. van Wüllen, *J. Chem. Phys.* **103**, 3589 (1995).  
<sup>19</sup>T. Ziegler, V. Tschinke, E. J. Baerends, J. G. Snijders, and W. Ravenek, *J. Phys. Chem.* **93**, 3050 (1989).  
<sup>20</sup>D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, and H. Preuss, *Theor. Chim. Acta* **77**, 123 (1990).  
<sup>21</sup>(a) K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules* (Van Nostrand, New York, 1979); (b) C. A. Stearns and F. J. Kohl, *J. Phys. Chem.* **77**, 136 (1973).  
<sup>22</sup>(a) G. L. Malli and N. C. Pyper, *Proc. R. Soc. London, Ser. A* **407**, 377 (1986); (b) G. L. Malli, in *The Transactinide Elements* (Proceedings of the Robert A. Welch Foundation Houston, TX, 1997), p. 197.  
<sup>23</sup>C. L. Collins, K. G. Dyall, and H. F. Schaefer, *J. Chem. Phys.* **102**, 2024 (1995).  
<sup>24</sup>(a) P. Schwerdtfeger, T. Fischer, M. Dolg, G. Igel-Mann, A. Nicklass, H. Stoll, and A. Haaland, *J. Chem. Phys.* **102**, 2050 (1995); (b) T. Leininger, A. Nicklass, H. Stoll, M. Dolg, and P. Schwerdtfeger, *ibid.* **105**, 1052 (1996).  
<sup>25</sup>R. Brown, J. K. Laerdahl, and P. Schwerdtfeger (unpublished).  
<sup>26</sup>M. D. Morse, *Chem. Rev.* **86**, 1049 (1986).  
<sup>27</sup>C. W. Finley and J. Ferrante, *Surf. Interface Anal.* **24**, 133 (1996).  
<sup>28</sup>P. Schwerdtfeger, *Mol. Phys.* **86**, 359 (1995).  
<sup>29</sup>W. Kuechle, M. Dolg, H. Stoll, and H. Preuss, *Mol. Phys.* **74**, 1245 (1991).  
<sup>30</sup>(a) S. G. Lias, J. F. Liebman, R. D. Levin, and S. A. Kafafi, NIST Standard Reference Database, Positive Ion Energetics, Version 2.01, January 1994; (b) H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **14**, 731 (1985); (c) N. D. Gibson, B. J. Davies, and D. J. Larson, *J. Chem. Phys.* **98**, 5104 (1993).  
<sup>31</sup>M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, J. Baker, J. J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, *Program GAUSSIAN94, Rev. D.1* (Gaussian, Pittsburgh, PA, 1996).  
<sup>32</sup>J. F. Stanton, J. Gauss, J. D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W. L. Lauderdale, S. R. Gwaltney, S. Beck, A. Balková, D. E. Bernholdt, K.-K. Baeck, H. Sekino, and R. J. Bartlett, *Program ACESII* (University of Florida, Gainesville, 1995).  
<sup>33</sup>K. Andersson, M. R. A. Blomberg, M. P. Fülscher, V. Kellö, R. Lindh, P.-Å. Malmqvist, J. Noga, J. Olsen, B. O. Roos, A. J. Sadlej, P. E. M. Siegbahn, M. Urban, and P. O. Widmark, *Program VIBROT*, implemented in MOLCAS, Version 2, University of Lund, Sweden, 1991.  
<sup>34</sup>T. Saue, T. Enevoldsen, T. Helgaker, H. J. A. Jensen, J. K. Laerdahl, K. Ruud, J. Thyssen, and L. Visscher, *Dirac: A Relativistic ab initio Electronic Structure Program*, Odense, Denmark, 1998.  
<sup>35</sup>J. K. Laerdahl, T. Saue, and K. Faegri, Jr., *Theor. Chem. Acc.* **97**, 177 (1997).  
<sup>36</sup>J. K. Laerdahl, K. Faegri, Jr., L. Visscher, and T. Saue, *J. Chem. Phys.* **109**, 10806 (1998).  
<sup>37</sup>J. Thyssen and H. J. A. Jensen (unpublished).  
<sup>38</sup>L. Visscher, T. J. Lee, and K. G. Dyall, *J. Chem. Phys.* **105**, 8769 (1996).

- <sup>39</sup>L. Visscher and K. G. Dyall, *At. Data Nucl. Data Tables* **67**, 207 (1997).
- <sup>40</sup>T. Saue, J. K. Laerdahl, L. Visscher, and H. J. A. Jensen (unpublished).
- <sup>41</sup>(a) I. P. Grant and H. M. Quiney, *Adv. At. Mol. Phys.* **23**, 37 (1988); (b) K. G. Dyall and K. Faegri, Jr., *Chem. Phys. Lett.* **174**, 25 (1990).
- <sup>42</sup>D. Dai and K. Balasubramanian, *J. Chem. Phys.* **100**, 4401 (1994).
- <sup>43</sup>R. Wesendrup, T. Hunt, and P. Schwerdtfeger (to be published).
- <sup>44</sup>C. E. Moore, *Atomic Energy Levels*, Circ. No. 467 (U.S. Government Printing Office, National Bureau of Standards, U.S. GPO Washington, DC, 1958).
- <sup>45</sup>(a) P. Pyykkö, *J. Am. Chem. Soc.* **117**, 2067 (1995); (b) J. P. Read and A. D. Buckingham, *ibid.* **119**, 9010 (1997); (c) D. Schröder, H. Schwarz, J. Hrusak, and P. Pyykkö, *Inorg. Chem.* **37**, 624 (1998).